

Crystal structures and stability of NaLnF₄ (Ln = La, Ce, Pr, Nd, Sm, and Gd) studied with synchrotron single-crystal and powder diffraction

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The most efficient host material for green and blue upconversion known to date is hexagonal NaYF₄ doped with lanthanides [1]. It is widely used, for instance, in optical fibers, solar cells, and immunoassay detectors. Different synthesis methods and upconversion processes in the bulk, nanocrystalline, and colloidal material have been extensively studied over last decades. Efficient upconversion is also observed in various other MXF₄ host lattices (M = Li, Na, or K; X = rare earth or Y).

The high efficiency of the upconversion in the NaXF₄ compounds is related to the multisite character of their crystal structure [1-3]. The average structure of the NaXF₄ compounds at room temperature, i.e., of the β polymorphs, is described in space group $P\bar{6}$ [4]. Three cationic sites (Wyckoff positions WP) can be distinguished. Two of them [WP1f and WP1a] are coordinated by nine F ions forming capped trigonal prisms around X³⁺. The site [WP1f] shows occupational disorder and is populated by Na⁺ and X³⁺ in the ratio of 1:1. The site [WP1a] is fully occupied by X³⁺. The third cationic site [WP2h] with an irregular octahedral coordination is only half occupied by Na⁺.

The β phases with Y and heavier lanthanides transform to the fluorite-type α structure (space group Fm $\bar{3}$ m) at about 900-1000 K [5]. The actual transition temperature depends on the size of the X³⁺ cation. In contrast to the hexagonal phases, where partial ordering of the cations exists, the cubic α phases are characterized by complete cationic disorder.

In this study we were interested in further structural investigations of the β -NaLnF₄ compounds (Ln = La, Ce, Pr, Nd, Sm, or Gd) at ambient and high pressures using synchrotron radiation. The high brilliance of synchrotron radiation has the advantage of the improved peak to background ratio. It facilitates the detection of weak superstructure reflections that are difficult to be observed on a home diffractometer. In addition, the use of synchrotron radiation allows measurements at higher energies, when compared to the laboratory sources, and thus facilitates access to a larger fraction of the reciprocal space in the high-pressure single-crystal experiments using diamond anvil cells.

The single-crystal experiments at ambient ($\lambda = 0.3978$ Å) and high pressures ($\lambda = 0.4000$ Å) were performed on the beamline D3 at HASYLAB equipped with a HUBER four-circle diffractometer and a marCCD165 detector. For all the single-crystal measurements, the intensities were indexed and integrated using the program XDS [6]. Structure refinements were carried out with the program Jana2006 [7]. Powder x-ray measurements at high pressures and room temperature were also carried out using the same diffractometer and detector on the beamline D3. The images were integrated with the program FIT2D to yield intensity versus 2θ diagrams [8].

The datasets for Ln = La, Ce, Nd, Sm, and Gd measured at ambient pressure can be indexed with unit cells of approximately $a \sim 6.1 \text{ \AA}$ and $c \sim 3.8 \text{ \AA}$ [2]. On the other hand, in the dataset for NaPrF₄, weak superstructure reflections are observed. These additional reflections can be indexed with a large unit cell with $a = 10.617(1) \text{ \AA}$ and $c = 7.499(5) \text{ \AA}$. The transformation from the average structure to the larger superstructure cell is given by the following relationships: $a_{\text{super}} = a + 2b$, $b_{\text{super}} = a - b$, $c_{\text{super}} = 2c$; in a combination with an origin shift of $(2/3, 1/3, 0)$.

The compounds with Ln = La, Ce, Nd, Sm, and Gd crystallize in the β structure previously reported [2,9]. A new type of superstructure due to partial ordering of the Na⁺ and Pr³⁺ cations as well as of vacancies is observed in NaPrF₄. The structural model could be derived on the basis of group-subgroup relationships. The high-pressure studies using synchrotron powder and single-crystal diffraction in diamond anvil cells at room temperature demonstrate that β -NaNdF₄ and β -NaGdF₄ as well as the superstructure NaPrF₄ are stable on compression to at least 8 GPa.

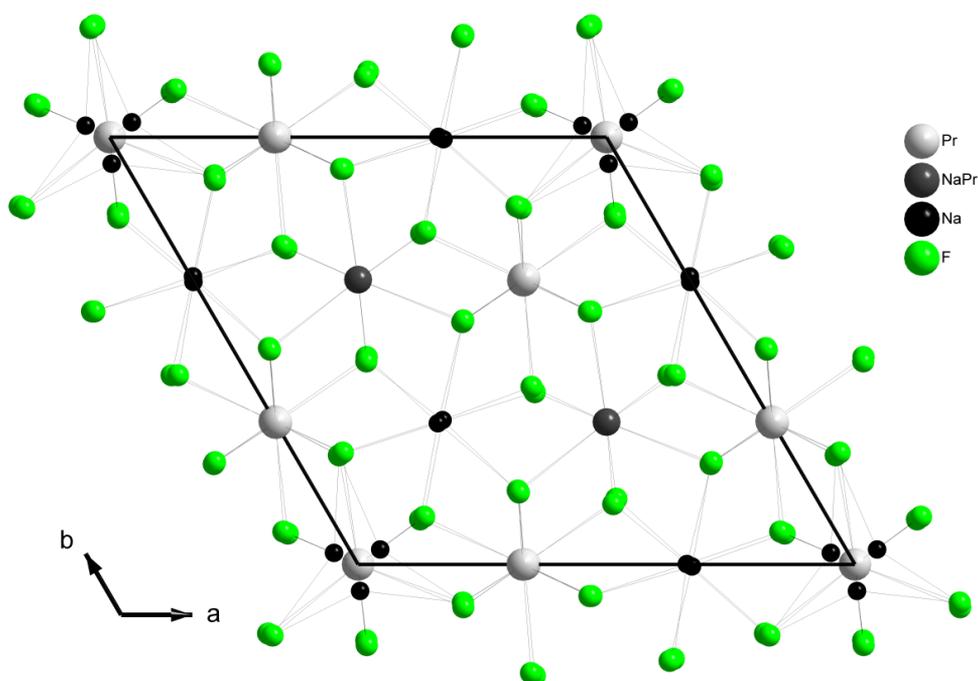


Figure 1. Crystal structure of NaPrF₄ at ambient pressure.

References

- [1] M. Haase and H. Schäfer, *Angew. Chem. Int. Ed.*, 2011, 50, 5808.
- [2] A. Aebischer, M. Hostettler, J. Hauser, K. Krämer, T. Weber, H.U. Göbel, H. B. Bürgi, *Angew. Chem. Intl. Ed.*, 2006, 45, 2802.
- [3] C. Renero-Lecuna, R. Martin-Rodriguez, R. Valiente, J. González, F. Rodriguez, K.W. Krämer, H.U. Güdel, *Chem. Mater.*, 2011, 23, 3442.
- [4] J. H. Burns, *Inorg. Chem.*, 1965, 4, 881.
- [5] R. E. Thoma, H. Insley, G. M. Herbert, *Inorg. Chem.*, 1966, 5, 1222.
- [6] W.Kabsch, *Acta Cryst. D*, 2010, 66, 125.
- [7] V. Petricek, M. Dusek and L. Palatinus, *JANA2006 – Crystallographic Computing System*, Institute of Physics, Academy of Sciences of the Czech Republic, Praha, 2006.
- [8] A.P. Hammersley, S.O. Svensson, M. Hanfland, A.N. Fitch, D. Hausermann, *High Press. Res.* 1996, 14, 235.
- [9] A. Grzechnik, P. Bouvier, M. Mezouar, M. D. Mathews, A. K. Tyagi, J. Köhler, *J. Solid State Chem.*, 2002, 165, 159.